On the Utilization of Higher Boiling Products from the Reaction between Methyl Chloride and Si-Cu

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Chemical analyses of several experimental slags.

Sample No.	Added Comps.	Chemical Components								
		Cu	Fe	Zn	SiO_2	Al_2O_3	CaO	MgO	BaO	S
1	None (Std. slag)	0.41	36.1	2.7	37.0	8.6	0.07	0.12	Tr.	0.5
2	+3% CaO	0.7	34.8	2.5	36.8	8.8	1.9	0.05	〃	0.8
3	+6% BaO	0.9	35.3	2.7	34.2	9.6	0.16	0.03	4.7	0.7
4	+9% MgO	0.8	36.0	2.7	35.4	8.1	0.16	2.2	Tr.	0.7
5	+6% Al_2O_3	0.8	35.4	2.5	34.9	12.6	0.07	0.1	〃	0.7

In Fig. 2, some of the measured viscosities of slags are shown.

The results were as follows.

1. By addition of CaO to some extent, viscosity decreases in Al_2O_3-FeO-SiO_2 slags as in the CaO-Al_2O_3-SiO_2 and CaO-FeO-SiO_2 slags.

2. By addition of BaO, viscosity of slags somewhat increases in temperature range from 1200° to 1100°C.

3. It is said that an addition of MgO increases viscosity in the CaO-FeO-SiO_2 slags, and decreases in the CaO-Al_2O_3-SiO_2 slags. In the present experiment, viscosity seems to decrease a little at high temp., and somewhat increases at low temp. in the Al_2O_3-FeO-SiO_2 slags.

4. Viscosity of all sorts of slags seems to increases with increasing Al_2O_3 content.

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17. On the Utilization of Higher Boiling Products from the Reaction between Methyl Chloride and Si-Cu

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One of the authors (M.Kumada and M.Yamaguchi, *J. Chem. Soc., Japan* (*Industrial Section*), in press) previously reported that the distillation residue of methylchlorosilanes resulting from the reaction of methyl chloride with Si-Cu mainly consists of the three types of compounds: methyl-chloro-disiloxanes, -disilanes and -disilmethylenes.

The present research was performed in order to have more detailed information concerning the compounds included in the disiloxane fraction (fraction of b.p.ca. 100–150°C, mainly composed of disiloxanes).

At first, this fraction was caused to react with ethylmagnesium bromide, to substitute the contained Cl with ethyl radical, since it was difficult to separate the compounds containing Cl in that condition, and then this ethylated products were treated

with cold conc. sulfuric acid in a similar manner to that previously reported. By this treatment, the disiloxanes could readily be separated from the substances having no Si-O group.

The fractional distillation of the liquid products recovered from the sulfuric acid solution gave essentially two compounds: tetramethyldiethyldisiloxane (I) and trimethyltriethyldisiloxane (II) as shown in Fig. 1 and Table I. The former appears

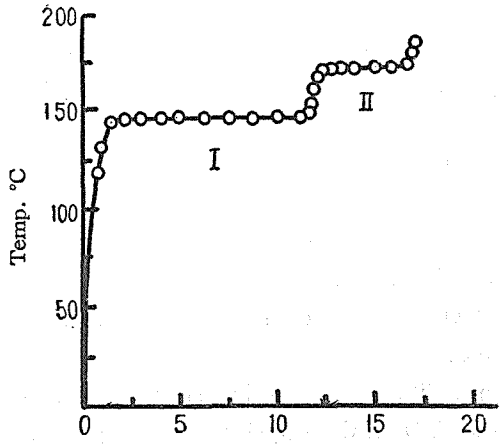

Fig. 1.

Table 1.

No.	Formula	B.P. °C	d_4^{20}	n_D^{20}	MR_D		%Si	
					calcd.	Found	Calcd.	Found
I	$Me_4Et_2Si_2O$	147.0-147.5 (152)[a]	0.7967 (0.798)[a]	1.4017 (1.4000)[a]	58.18	58.46	29.3	29.0
II	$Me_3Et_3Si_2O$[b]	170.5-170.9	0.8053	1.4097	62.81	62.85	27.5	26.8
III	Me_2Et_2Si	96 (96.0)[c]	—	—	—	—	24.1	24.1
IV	$MeEt_3Si$	127 (127)[d]	—	1.4163 (1.4160)[d]	—	—	21.5	20.1

[a] Dow Corning, Brit. Pat. 659012 : *C.A.*, **46**, 4853e.
[b] New compound.
[c] A. Bygden, *Ber.*, 44 B 2460 (1911).
[d] F.C. Whitmore, et al., *J. Am. Chem. Soc.*, **68**, 475 (1946).

to be tetramethyl-1, 3-diethyldisiloxane in comparison of its physical properties with those in the literature. Further investigation, however, e.g., a performance of the Flood reaction (E.A. Flood, *J. Am. Chem. Soc.*, **55**, 1735 (1933)), is necessary for conclusive identification of these compounds. Each methylethyldisiloxane thus obtained might not necessarily correspond to the respective methylchlorodisiloxane prior to ethylation, since the rearrangement of siloxane bond is well known to take place in the presence of sulfuric acid (W.I. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*,

68, 358 (1946); F. P. Price, *ibid.*, 70, 871 (1949)).

There were obtained, on the other hand, dimethyldiethylsilane (III) and methylthylriet silane (IV) as shown in Fig. 2 and Table 1, instead of the disilane derivatives,

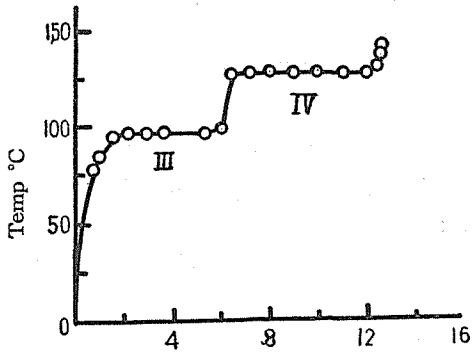

Fig. 2

the fractional distillation of the sulfuric acid-insoluble layer. This apparently unexpected result is probably due to the fission of Si-Si bond in 1, 1, 2-trimethylchlorodisilane, for example, during the Grignad reaction under the conditions employed. Similar phenomena have been already recognized by the several researchers (cf. Krause and von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin 1937, p. 268).

From these results, it is known that the compounds containing methyldichlorosilyl and dimethylchlorosilyl radicals exist in this disiloxane fraction.

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18. Studies on Acetylene and its Derivatives. (XII)

Reactions of Aldehydes and Acetylene under Pressure. (2)

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Acetylene was reacted with formaldehyde under pressure using various catalysts, and in order to obtain a superior amount of propargyl alcohol, the selective conditions were investigated.

The following Cu catalysts were used, and the general experimental procedures were similar to that of previous report (read at the 6th annual meeting of Chem. Soc. of Japan).

(A) Single catalysts:

The catalysts were prepared from the following materials.